

## Electronic supplementary information

# Ionothermal synthesis and magnetic study of a new manganese(II) phosphite with an unprecedented Mn/P ratio

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## Experiment:

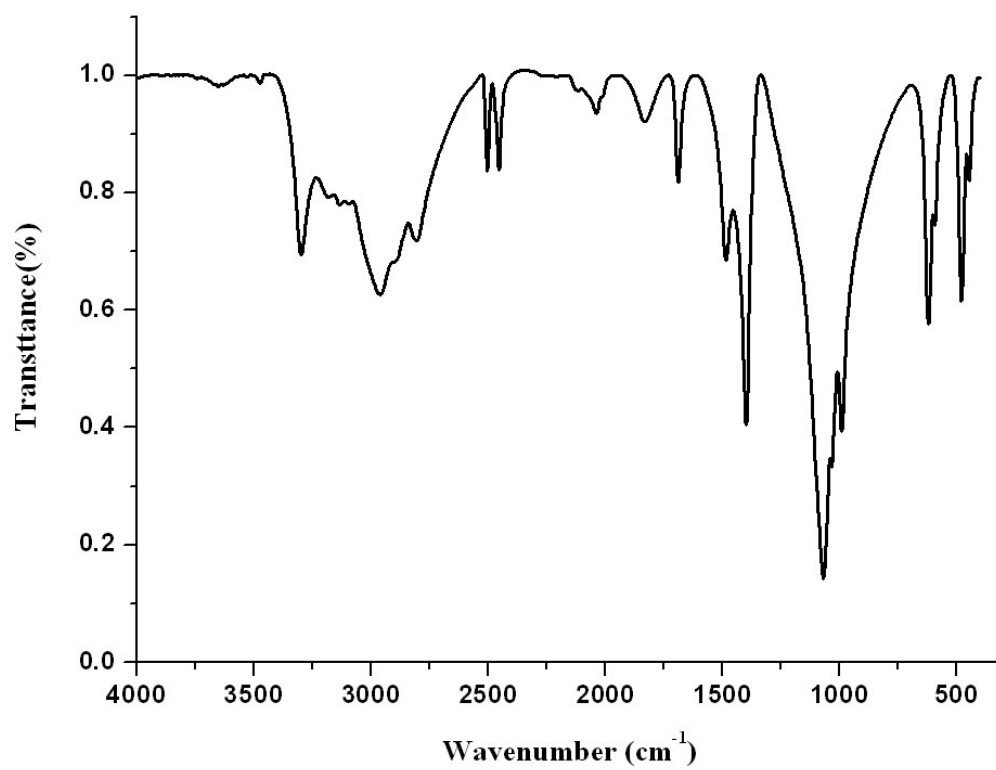
JIS-10 was prepared under ionothermal conditions using the ionic liquid [Pmim]Br as the solvent. Other chemicals including  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_3$ , and  $\text{NH}_4\text{F}$  were used as received in reagent grade. Hexagonal-prism-shaped pink crystals of JIS-10 with a yield of  $\sim 70\%$  (based on Mn) were obtained from a reaction mixture of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.07 g, 0.35 mmol),  $\text{H}_3\text{PO}_3$  (0.30 g, 3.66 mmol), [Pmim]Br (1 mL, 5.09 mmol) and  $\text{NH}_4\text{F}$  (0.15 g, 4.05 mmol). The reaction mixture was heated in a 15-mL Teflon-lined autoclave under autogenous pressure at 150 °C for 7 days and cooled to room temperature within 3 hours. Ion-exchange experiment was carried out by sealing 0.030g of JIS-10 sample and KBr liquid (20%) in a microwave autoclave and heating at 80 °C for 25 min.

## Characterisation:

A single crystal of JIS-10 with dimensions of  $0.16 \times 0.13 \times 0.11 \text{ mm}^3$  was selected for single-crystal X-ray diffraction analysis. The data were recorded using a Bruker AXS SMART APEX II diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a room temperature. Data processing was accomplished using the SAINT processing program. The structure of JIS-10 was solved in space group  $P6_3/mmc$  via direct methods and refined with a full matrix least-squares technique implemented in SHELXTL software package. All non-hydrogen atoms were refined anisotropically. More detailed information could be found in the CIF file deposited at CCDC (1441924). Because of the existence of the mirror plane perpendicular to the  $6_3$  axis in space group  $P6_3/mmc$ , one of the two P atoms was found disordered. Attempts to refine the structure of JIS-10 in non-centrosymmetric space group  $P6_3mc$  with TWIN-BASF instructions were also made. Although the refinement in  $P6_3mc$  avoided the disordered P atom, it led to obviously worse  $R$  indices than the refinement in  $P6_3/mmc$ . Besides, two of three O atoms in  $P6_3mc$  became non-positive-definite when their anisotropic displacement parameters were refined. H atoms were also difficult to locate in  $P6_3mc$ . Because of these reasons, we chose space group  $P6_3/mmc$  to elucidate the structure of JIS-10.

In situ temperature-dependent X-ray diffraction data were collected on a Rigaku D-Max 2550 diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a rate of  $4^\circ \text{ min}^{-1}$ . The heating rate was  $10^\circ \text{ C min}^{-1}$ . The powder X-ray diffraction pattern of JIS-10 was consistent with that calculated from single crystal data. Inductively coupled plasma analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Thermogravimetric analysis was carried out on a TA Q500 analyser in air at a heating rate of  $10^\circ \text{ C min}^{-1}$ . Infrared analysis was performed on a Bruker IFS 66v/S FTIR spectrometer. The C, H, and N contents were determined on a Perkin-Elmer 2400 elemental analyser.

The DC and AC magnetic susceptibilities of the powder sample were measured using a Quantum-Design MPMS-XL SQUID magnetometer. For the DC measurements, the data were collected over the temperature range from 4 to 300 K, both after cooling in zero applied field (ZFC) under the measuring field 50 kOe (FC). The AC measurements were carried out at zero field with the ac modulation amplitude of 2 Oe and the frequency between 1 to 1000 Hz.



**Fig. S1** IR spectrum of JIS-10

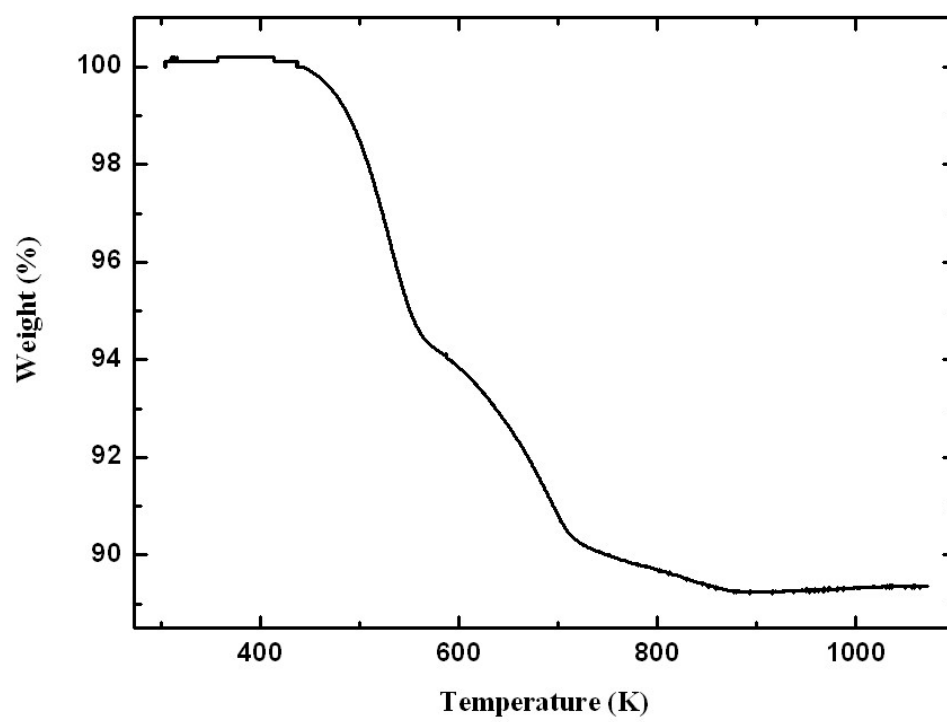
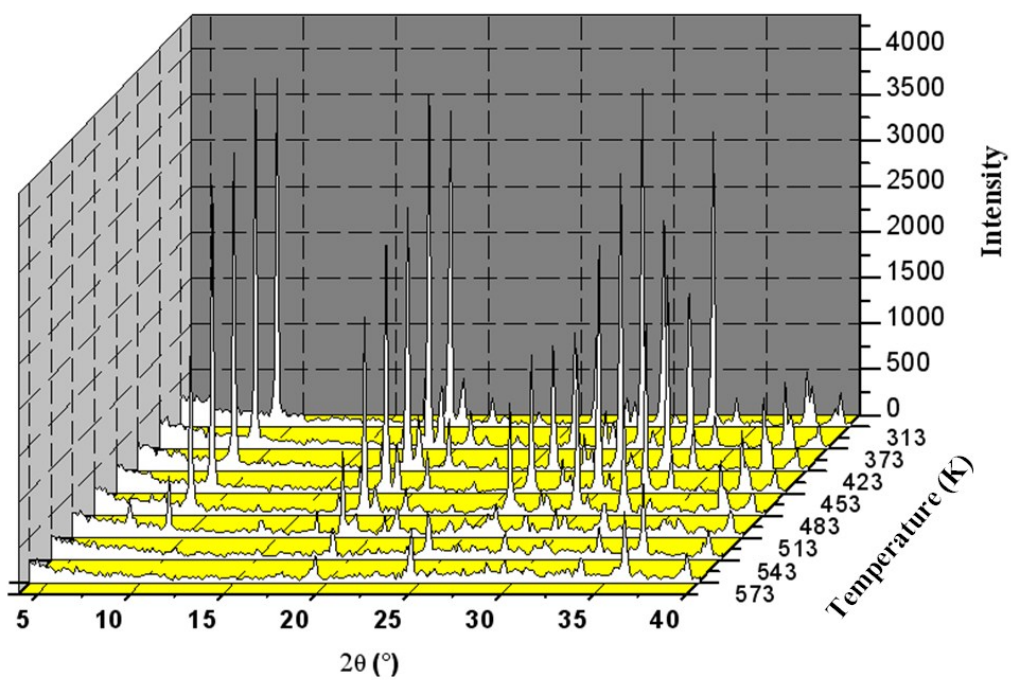
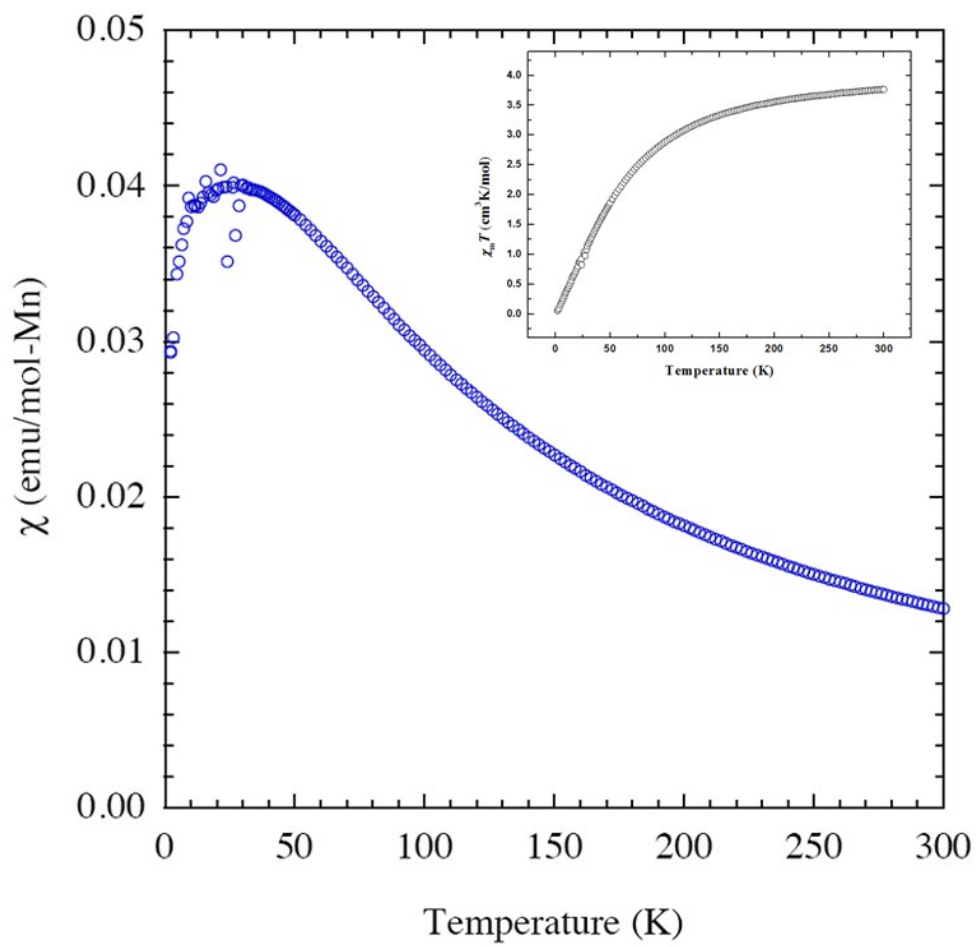


Fig. S2 Thermogravimetric curve of JIS-10



**Fig. S3** In-situ temperature-dependent powder X-ray diffraction patterns of JIS-10



**Fig S4.**  $\chi$  vs  $T$  curve of JIS-10. The inset is the curve of  $\chi T$  vs  $T$  under 5 T.

**Table S1.** The manganese phosphites with various Mn/ P ratios reported to date.

Chemical formula	Mn : P	Year
$\text{MnHPO}_3 \cdot 3.6 \text{H}_2\text{O}$	1:1	1827
$\text{MnH}_4\text{P}_2\text{O}_6 \cdot \text{H}_2\text{O}$	1:2	1965
$\text{Mn}_3\text{H}_6\text{P}_4\text{O}_{12} \cdot 1.5 \text{H}_2\text{O}$	3:4	1974
$\text{Mn}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 4\text{H}_2\text{O}$	2:5	1974
$\text{Mn}_2\text{H}_{17}\text{P}_7\text{O}_{21} \cdot 4\text{H}_2\text{O}$	2:7	1974
$\text{MnH}_{10}\text{P}_4\text{O}_{12} \cdot \text{H}_2\text{O}$	1:4	1974
$\text{Mn}_{11}(\text{HPO}_3)_8(\text{OH})_6$	11:4	1994
$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Mn}_3(\text{HPO}_3)_4]$	3:4	2000
$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Mn}_3(\text{HPO}_3)_4]$	3:4	2001
$\text{Mn}(\text{HPO}_3)$	1:1	2005
$[\text{H}_2\text{CHBMA}][\text{Zn}_2\text{Mn}_{0.5}(\text{PO}_4)(\text{HPO}_3)_2] \cdot \text{H}_2\text{O}$	1:6	2009
$\text{K}_2[\text{Mn}_3(\text{HPO}_3)_4]$	3:4	2009
$[\text{C}_2\text{N}_2\text{H}_{10}][\text{Mn}_2(\text{OH})_2(\text{HPO}_3)_2(\text{C}_2\text{O}_4)]$	1:1	2009
$\text{Mn}_{11}(\text{HPO}_3)_8(\text{OH})_6$	11:8	2010
$(\text{NH}_4)_7\text{Mn}_4(\text{H}_2\text{O})[\text{B}_2\text{P}_4\text{O}_{15}(\text{OH})_2]_2[\text{H}_2\text{PO}_4][\text{HPO}_4]$	2:5	2012
$(\text{CN}_3\text{H}_6)_2 \cdot \text{Mn}_{2.5}(\text{HPO}_3)(\text{C}_2\text{O}_4)_{2.5}(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$	5:2	2014
$(\text{NH}_4)_2 \text{Mn}_3(\text{HPO}_3)_4, \text{Mn}(\text{HPO}_3)$	3:4, 1:1	2014
$(\text{NH}_4)_4[\text{Mn}_4(\text{HPO}_3)_6]$	2:3	This work

**Table S2.** Selected bond lengths [Å] and angles [°] in JIS-10.

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Mn(1)-O(2)#1	2.148(4)
Mn(1)-O(2)	2.148(4)
Mn(1)-O(2)#2	2.148(4)
Mn(1)-O(1)	2.265(4)
Mn(1)-O(1)#1	2.265(4)
Mn(1)-O(1)#2	2.265(4)
P(1)-P(1)#3	0.617(7)
P(1)-O(1)#4	1.516(6)
P(1)-O(1)#5	1.516(6)
P(1)-O(1)	1.516(6)
P(1)-H(1)	1.33(5)
P(2)-O(2)#6	1.511(4)
P(2)-O(2)	1.511(4)
P(2)-O(2)#7	1.511(4)
P(2)-H(2)	1.34(5)
O(1)-P(1)#3	1.516(6)
O(1)-Mn(1)#3	2.265(4)
N(1)-H(3)	0.97(8)
N(1)-H(4)	0.98(14)
O(2)#1-Mn(1)-O(2)	87.34(16)
O(2)#1-Mn(1)-O(2)#2	87.34(16)
O(2)-Mn(1)-O(2)#2	87.34(16)
O(2)#1-Mn(1)-O(1)	96.50(11)
O(2)-Mn(1)-O(1)	96.50(11)
O(2)#2-Mn(1)-O(1)	174.68(16)
O(2)#1-Mn(1)-O(1)#1	96.50(11)
O(2)-Mn(1)-O(1)#1	174.68(16)
O(2)#2-Mn(1)-O(1)#1	96.50(11)
O(1)-Mn(1)-O(1)#1	79.44(16)
O(2)#1-Mn(1)-O(1)#2	174.68(16)
O(2)-Mn(1)-O(1)#2	96.50(11)
O(2)#2-Mn(1)-O(1)#2	96.50(11)
O(1)-Mn(1)-O(1)#2	79.44(16)
O(1)#1-Mn(1)-O(1)#2	79.44(16)
O(1)#4-P(1)-O(1)#5	115.97(10)
O(1)#4-P(1)-O(1)	115.97(10)
O(1)#5-P(1)-O(1)	115.97(10)
O(1)#4-P(1)-H(1)	101.73(14)
O(1)#5-P(1)-H(1)	101.73(14)
O(1)-P(1)-H(1)	101.73(14)

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O(2)#6-P(2)-O(2)	111.50(15)
O(2)#6-P(2)-O(2)#7	111.50(15)
O(2)-P(2)-O(2)#7	111.50(15)
O(2)#6-P(2)-H(2)	107.36(17)
O(2)-P(2)-H(2)	107.36(16)
O(2)#7-P(2)-H(2)	107.36(16)

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Symmetry transformations used to generate equivalent atoms:

#1  $-x+y+1, -x+1, z$     #2  $-y+1, x-y, z$     #3  $x, y, -z+1/2$   
#4  $-x+y+2, -x+2, z$     #5  $-y+2, x-y, z$     #6  $-y+2, x-y+1, z$   
#7  $-x+y+1, -x+2, z$

**Table S3.** Hydrogen bonds in JIS-10 [ $\text{\AA}$  and  $^\circ$ ].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(3)...O(2)#8	0.97(8)	2.17(6)	3.014(4)	144.8(12)
N(1)-H(3)...O(2)#9	0.97(8)	2.17(6)	3.014(4)	144.8(12)
N(1)-H(4)...O(2)#1	0.98(14)	2.36(10)	3.110(8)	133(2)
N(1)-H(4)...O(2)#2	0.98(14)	2.36(10)	3.110(8)	133(2)
N(1)-H(4)...O(2)	0.98(14)	2.36(10)	3.110(8)	133(2)

Symmetry transformations used to generate equivalent atoms:

#1  $-x+y+1, -x+1, z$     #2  $-y+1, x-y, z$     #3  $x, y, -z+1/2$   
#4  $-x+y+2, -x+2, z$     #5  $-y+2, x-y, z$     #6  $-y+2, x-y+1, z$   
#7  $-x+y+1, -x+2, z$     #8  $y, -x+y+1, -z+1$     #9  $x-y+1, x, -z+1$